



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification<sup>6</sup> :  <b>C02F 1/52, 1/54, C08F 34/00</b></p>	<p><b>A1</b></p>	<p>(11) International Publication Number: <b>WO 99/19262</b>                  (43) International Publication Date: 22 April 1999 (22.04.99)</p>
<p>(21) International Application Number: PCT/US98/21791                  (22) International Filing Date: 15 October 1998 (15.10.98)                  (30) Priority Data:                          60/062,119                      15 October 1997 (15.10.97)              US                          09/053,813                      2 April 1998 (02.04.98)                      US                  (71) Applicant: CPS CHEMICAL COMPANY, INC. [US/US]; 900 Route 9 North, Woodbridge, NJ 07095-1015 (US).                  (72) Inventors: SCHRIVER, George, W.; 488 Auten Road #4C, Somerville, NJ 08876 (US). EASTER, Darrel, E.; 3165 Woodsman Lane, Bartlett, TN 38135 (US). YUN, Han, Bo; 16 Landing Lane, Princeton Junction, NJ 08550 (US). PADEGIMAS, Stanley; 3143 Arbor Grove Way, Memphis, TN 38119 (US).                  (74) Agent: BUTCH, Peter, J., III; Synnestvedt &amp; Lechner LLP, 2600 Aramark Tower, 1101 Market Street, Philadelphia, PA 19107-2950 (US).</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b>  <i>With international search report.</i></p>
<p>(54) Title: CHAIN EXTENDED CATIONIC POLYMER SYNTHESIS</p> <p>(57) Abstract</p> <p>Methods for the solution polymerization of diallyldialkylammonium salts, initiated by species capable of generating free radicals, including the steps of providing a reaction mixture of a diallyldialkylammonium salt and a chain-extending monomer in aqueous solution at concentrations effective to polymerize to form a polydiallyldialkylammonium salt having a predetermined molecular weight; adding a free radical initiator to the reaction mixture; heating the reaction mixture with continuous stirring to a temperature greater than about 70 °C, so that the diallyldialkylammonium salt and the chain-extending monomer polymerize to form a polydiallyldialkylammonium salt; and recovering the polydiallyldialkylammonium salt in aqueous solution; wherein the alkyl groups of the diallyldialkylammonium salt and the polydiallyldialkylammonium salt contain a total of from two to eight carbons atoms. Aqueous solutions of polydiallyldialkylammonium salts prepared by the polymerization method, and methods for the separation of suspended particles from an aqueous medium with aqueous solutions of the polydiallyldialkylammonium salts are also disclosed.</p>		

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## CHAIN EXTENDED CATIONIC POLYMER SYNTHESIS

### CROSS-REFERENCE TO RELATED APPLICATION

5 The present application claims priority benefit of U.S. Provisional Patent Application Serial No. 60/062,119 filed on October 15, 1997. The present application also claims priority benefit of U.S. Patent Application Serial No. 09/053,813 filed April 2, 1998. The disclosures of both applications are incorporated herein by reference.

### TECHNICAL FIELD

10 The present invention relates to methods for polymerizing diallyldialkylammonium salts employing chain-extending monomers, in which the chain-extending monomer is added in the initial polymer charge. The present invention also relates to polydiallyldialkylammonium salts prepared by the methods of the present invention, and methods of aggregating particles suspended in aqueous media using the polydiallyldialkylammonium salts  
15 of the present invention. The present invention particularly relates to the polymerization of diallyldimethylammonium chloride (DADMAC) and the uses of this polymer.

### BACKGROUND ART

20 Cationic polymers are used in a variety of applications, primarily for coagulating and flocculating fine particles in aqueous solutions. Among these, polymers of diallyldimethylammonium salts are particularly efficient coagulants. Recent industry trends have been toward the production of higher molecular weight polydiallyldimethylammonium chlorides (polyDADMACs). In many cases, higher molecular weights leads to improved performance.

25 The most common preparation of polydiallyldialkylammonium salts is by solution polymerizing using free-radical initiators. Ammonium persulfate is a common initiator. Some properties of the diallyldialkylammonium salt monomer are not well suited to polymerization to high molecular weight. Notably, hydrogen abstraction from the diallylic-

dialkylammonium salt monomer or from the polymer can give chain transfer, limiting molecular weight. It has also been claimed that the chloride ion in DADMAC in particular can be oxidized by persulfate ion to give atomic chlorine, a potent chain terminator. For these reasons, preparation of higher molecular weight polydiallyldialkylammonium salts has proven difficult.

Some standard methods of increasing the molecular weight of polydiallyldialkylammonium salts include raising the initial concentration of the diallyldialkylammonium salt monomer and performing the polymerization at lower temperatures. Both of these techniques increase the likelihood of chain propagation reactions relative to chain termination or chain transfer reactions. Thus, the average molecular weight of the polymer is increased. These techniques also lead to an increase in the viscosity of the polymerizing mixture. Associated with this, there can be poor mixing and poor distribution of the free-radical initiator, leading to inconsistent molecular weight and the formation of color bodies or polymer gels. These are undesirable attributes in polymer products.

There are other types of polymerization in which this viscosity problem does not obtain. Diallyldialkylammonium salts can be polymerized as a water-in-oil emulsion, or as a suspension of monomer droplets. In these cases, the developing polymer is confined to individual droplets separated by an oleaginous phase. Entanglement of the polymer throughout the reaction medium, with its attendant stirring problems is not observed.

Another approach to making high molecular weight solution polymers is copolymerization with small amounts of monomers capable of multiple reaction. These added species are called crosslinkers or chain extenders. They serve to increase the molecular weight of the polymer by chemically linking several polymer chains, either during or after their formation. In common usage, crosslinking often refers to situations where

multiple connections between polymer chains are formed, leading to insoluble polymer gels. When fewer of these interconnections are made, the process is sometimes referred to as chain extension. Here, the polymer attains a higher molecular weight, but its basic chemical properties do not differ greatly from those of the polymer that would be obtained in the absence of the chain extender.

Chain extenders have been used in emulsion and suspension polymerization. *Kerr et al.*, U.S. Patent No. 5,653,886, have reported the use of chain extenders in emulsion polymerization including homopolymerization of DADMAC. *Flesher et al.*, U.S. Patent No. 4,950,725, have reported the use of chain extenders in emulsion polymerization including homopolymerization of DADMAC.

In previously disclosed art (EP 264,710), *W. Jaeger et al.* have used chain extenders to produce higher molecular weight solution polyDADMACs. The procedures explicitly require that the chain extender be added to the polymerizing mixture through the course of reaction, beginning after a certain amount of conversion has occurred. A process wherein the chain extender need not be added throughout the course of the reaction would be highly desirable.

## SUMMARY OF THE INVENTION

This need is met by the present invention. A process has been discovered whereby the chain extender can be added with the monomer in the initial polymer charge, avoiding the necessity of continuous feed.

Therefore, according to one aspect of the present invention, a method is provided for the solution polymerization of diallyldialkylammonium salts, initiated by species capable of generating free radicals, which method includes the steps of:

providing a reaction mixture of a diallyldialkylammonium salt and a chain-extending monomer in aqueous solution at

concentrations effective to polymerize to form a polydiallyldialkylammonium salt having a predetermined molecular weight;

adding a free radical initiator to the reaction mixture;

heating the reaction mixture with continuous stirring to

5 a temperature greater than about 70°C, so that the diallyldialkylammonium salt and the chain-extending monomer polymerize to form a polydiallyldialkylammonium salt; and

recovering the polydiallyldialkylammonium salt in aqueous solution;

10 wherein the alkyl groups of the diallyldialkylammonium salt and the polydiallyldialkylammonium salt contain a total of from two to eight carbon atoms.

The method of the present invention is particularly advantageous in the preparation of higher molecular weight polyDADMAC  
15 from DADMAC.

While not being bound by any particular theory, it is believed that the method of the present invention results in the formation of polydiallyldialkylammonium salts with a unique polymer branching distribution because all of the chain-extending monomer is introduced at the  
20 beginning of the reaction. Because in *Jaeger's* polymerization, the chain extender is added later in the polymerization, the branches which are produced by the chain extender are in general of shorter length, giving those polymers different geometric properties from the polymers of the present invention.

25 Therefore, according to another aspect of the present invention, polydiallyldialkylammonium salts are provided, which are prepared by the method of the present invention. Such polydiallyldialkylammonium salts preferably have a bulk viscosity greater than about 3,000 cps at about 20 percent solids, measured by a Brookfield viscometer

using a No. 4 spindle at 30 rpm and 25°C. The preferred polydiallylicdialkylammonium salt is polyDADMAC.

The unique branching of the polymers of the present invention makes them particularly suitable for the removal of suspended particles in an aqueous medium. Therefore, according to another aspect of the present invention, a method is provided for the separation of suspended particles from an aqueous medium, which method includes the steps of:

adding an aqueous solution of a polydiallylicdialkylammonium salt prepared by the method of the present invention to the aqueous medium in an amount effective to provide a polymer concentration of at least about 0.01 weight percent, so that agglomerates of the polydiallylicdialkylammonium salt and the suspended particles are formed; and

separating the agglomerates from the aqueous medium.

Lower molecular weight species of the polydiallylicdialkylammonium salt agglomerate the suspended particles by coagulation, while higher molecular weight species agglomerate the suspended particles by flocculation. Polymer species that are of intermediate molecular weight are believed to agglomerate the suspended particles by a hybrid coagulation-flocculation mechanism.

The particle agglomeration method of the present invention can be used in a number of industrial processes, which include, but are not limited to, potable and wastewater clarification, oily water separation, sludge dewatering, mineral processing, including coagulation of fines and clarification of process water, in paper making as a retention aid, among other uses, and the like.

In addition to particle coagulation and flocculation, the polydiallylicdialkylammonium salts of the present invention may also be applied to the other well-known end uses for polyDADMACs. Such end uses include, but are not limited to, textile dye binders and dye thickeners,

personal care applications, including shampoos, hair and skin conditioners, soaps and lotions, conductive coatings for paper, and the like.

5           Therefore, according to another aspect of the present invention, substrates are provided coated with a layer of polydiallyldialkylammonium salt prepared by the method of the present invention. The present invention also includes a method for preparing a coated substrate by forming on the substrate a layer of the aqueous solution of the polydiallyldialkylammonium salt prepared by the method of the present invention; and drying the layer. Paper is a particularly  
10 preferred substrate.

Other features of the present invention will be pointed out in the following descriptions and claims, which disclose the principles of the invention and the best modes which are presently contemplated for carrying them out.

## 15   **BEST MODES OF CARRYING OUT THE INVENTION**

The present invention incorporates the discovery that in polydiallyldialkylammonium salt polymerization processes employing chain-extending agents, the chain-extending agent can be added with the diallyldialkylammonium salt monomer in the  
20 initial polymer charge, avoiding the necessity of continuous feed. In order to add effective amounts of chain-extending agents in the initial polymer charge without giving rise to unacceptable amounts of insoluble gel, it has been found that polymerization at elevated temperatures is required. For purposes of the present invention, polydiallyldialkylammonium salts are defined as copolymers of a diallyldialkylammonium salt with a chain-extending  
25 monomer.

The process of the present invention polymerizes diallyldialkylammonium salt monomers having alkyl groups with a total of from two to eight carbon atoms to form the corresponding polydiallyldialkylammonium salts. For purposes of the present invention, the allylic



groups of the ammonium salts are defined as alkyl or aralkyl groups having from three to twelve carbon atoms and containing a site of ethylenic unsaturation separated from the ammonium nitrogen by a saturated carbon. Monomers in which both allylic groups are allyl groups are preferred. 5 Monomers having a total of two alkyl carbon atoms are also preferred. Although chloride salts are more common, other anionic groups can be used so long as the anion does not interfere with polymerization. The preferred monomer is DADMAC, which polymerizes to form polyDADMAC.

Any monomer capable of participating in two independent 10 polymerization chain reactions can, in principle, serve as the chain-extending monomer. These monomers are typically characterized by having two or more independent sites of ethylenic unsaturation, which is in contrast to diallyldialkylammonium salts, which have two sites of ethylenic unsaturation that do not function independently. Instead, they react together 15 in a cyclopolymerization, producing a dialkylpyrrolidinium ring incorporated in a single polymer chain.

Preferred chain-extending monomers are diallylicammonium salts with further sites of ethylenic unsaturation. Particularly preferred species include triallylmethylammonium chloride, triallylammonium 20 chloride, tetraallylammonium chloride and N,N,N',N'-tetraallyl(1,2)-ethylenediammonium chloride. Again, while chloride salts are more common, other anionic groups can be used so long as the anion does not interfere with polymerization. For example, triallylammonium acetate can be used in place of triallylammonium chloride.

25 Many other types of chain-extending monomers can also be used. Examples of other chain-extending monomers include, but are not limited to, acrylamides such as methylene bisacrylamide, acrylate and methacrylate esters such as ethylene glycol diacrylate or ethylene glycol

dimethacrylate, allyl compounds such as N,N'-diallyltartardiamide, and hybrid compounds such as allyl methacrylate.

Between about 35 and about 70 weight percent, and preferably between about 50 and about 60 weight percent, of a diallylicdialkyl-ammonium salt in aqueous solution is charged to a reactor with a small amount of the chain-extending monomer, typically between about 0.05 and about 3 percent by weight based on the charge of the diallylicdialkyl-ammonium salt, and preferably between about 0.10 and about 1.0 percent by weight. The chain-extending monomer can be in the form of a solid, neat liquid or aqueous solution.

The monomer concentration is adjusted to an appropriate amount by adding water or by removal of water. Among other factors, the monomer concentration is a determinant of the molecular weight of the polymer to be produced. The relationship between monomer concentration and molecular weight is well known to those skilled in the art, without undue experimentation.

The reactor charge is then deoxygenated. Polymerization is initiated by a free-radical initiator. Initiators may be fed through the course of the polymerization or introduced in one charge to begin polymerization. Suitable initiators include persulfate salts, azo compounds, organic peroxides and peresters, and hydrogen peroxide. In addition, two-component systems, often called redox systems, can be used. In these systems, the interaction of the two components produces free radicals which can initiate polymerization. An example of a redox system is sodium bromate and triethanolamine. For redox initiation systems, both components may be fed to the reactor, or one may be fed while the other is charged in its entirety before the beginning of polymerization.

The reaction mixture is mixed while the polymerization occurs. If needed, water can be added to dilute the polymerizing mixture so

that mixing is improved. In the case of initiators like persulfate salts, whose decomposition products are acidic, it may be necessary to adjust the pH during the course of the polymerization by adding an alkaline solution. The pH is preferably maintained between about 4 and about 7.

- 5           The polymerizing mixture is heated to ensure thorough mixing. The mixture should be heated to at least about 70°C, and preferably to temperatures above about 95°C. The polymerizing mixture can be heated to its reflux temperature.

          Upon completion of the reaction, the resulting polymer may be  
10   diluted by the addition of water, or concentrated by the removal of water, to a desired solids concentration. Residual monomer content can be reduced by post-treatment with reagents such as sodium bisulfite. The pH of the polymer solution can be adjusted to a desired value. The foregoing process steps are well known to those of ordinary skill in the art.

- 15           Another feature of the present invention is that the chain-extending monomer may be formed in situ by adding triallylamine to the monomer charge, followed by neutralization with an acid. For example, triallylammonium chloride may be prepared in situ by addition of triallylamine with the monomer charge, followed by neutralization with  
20   hydrochloric acid.

          The polymerization process yields aqueous polymer solutions having polymer molecular weights expressed in terms of bulk viscosity of at least 3,000 cps at about 20 percent solids, measured by a Brookfield viscometer using a No. 4 spindle at 30 rpm and 25°C. Viscosities ranging  
25   between about 3,400 and about 5,000 cps at 20 percent solids, measured in the same manner, have been obtained, and viscosities of at least about 6,000 cps at 20 percent solids are capable of being obtained through the routine optimization of reaction parameters.

Polymer solutions in accordance with the present invention typically have a solids concentration of between about 10 and about 30 weight percent. A solids concentration of about 20 weight percent is preferred. The polymer solutions exhibit an intrinsic viscosity between  
5 about 1 dL/g and 2 dL/g. The solutions have a Huggins constant between about 0.3 and about 0.7.

The present invention includes methods by which suspended particles are removed from aqueous media with the polymer solutions of the present invention through agglomeration. As noted above, depending upon  
10 the polymer molecular weight, the agglomeration is obtained by either coagulation, flocculation, or a combination of the two mechanisms.

For purposes of the present invention, the particles to be removed by the polymer solutions of the present invention include solid particles such as minerals, cellulosic or insoluble organic materials. Thus,  
15 the polymers of the present invention may be used for such uses as potable or waste water clarification, sludge dewatering, mineral processing, paper making or other such uses as are well known to those skilled in the art.

For purposes of the present invention, the particles to be removed by the polymer solutions of the present invention include fine  
20 droplets of non-polar organic materials, such as oils, the suspension of which in an aqueous medium is commonly referred to as an emulsion. Stated another way, the polymer solutions of the present invention can be used to demulsify emulsified oil and water mixtures.

The particle removal by agglomeration is performed using  
25 essentially conventional coagulation or flocculation techniques that are well known to those of ordinary skill in the art. The polymer solution is added to the aqueous media in an amount effective to provide a polymer concentration between about .005 and about 1 weight percent, and preferably between about 0.01 and about 0.1 weight percent. The

suspended particles are permitted to form polymer agglomerates. The aqueous medium may be agitated to increase the contact between the polymer in solution and the suspended particles. For the purposes of particle removal by agglomeration, polymers like those described in the present invention are often used in combination with other known coagulants and/or flocculants.

For purposes of the present invention, coagulation is defined as the neutralization of surface charge on particle surfaces, which charge causes the particles to repel each other rather than associating into larger particles which can more easily be separated. Flocculation is defined as an agglomeration mechanism by which individual higher molecular weight polymer molecules bind to multiple particles in suspension.

The flocculated agglomerates obtain a particle size that readily precipitates from the aqueous media, so that aqueous media essentially free of suspended particles may be recovered simply by decanting the supernatant liquid. Agglomerates formed by coagulation, on the other hand, are of a smaller particle size and do not precipitate so readily. More advanced separation techniques are employed to separate the agglomerates from the aqueous media, such as centrifugation, admixture of other solids such as clays or silica to bind the agglomerates, increasing their size and ease of separation, and the like. These techniques are well known to those of ordinary skill in the coagulation art, and may also be employed to accelerate the precipitation of flocculated agglomerates.

While not wishing to be bound by any particular theory, we conjecture that the crosslinking agent enters into polymerization along with the diallyldialkylammonium salt, but that even after adding to a growing polymer chain it still retains a site of ethylenic unsaturation. This site can undergo a second polymerization at a later time, linking two polymer chains, or providing a branch point from which two or more extensions of

the polymer chains can grow, thereby increasing molecular weight and polymer branching. The molecular weight of the final polymer will be governed by the molecular weights of the polymeric segments before their joining at the chain-extending sites and by the number of such joints that are made. Use of this theory can guide those skilled in the art to designing effective polymerization conditions for the production of polymers useful in the applications noted above.

The following non-limiting examples set forth hereinbelow illustrate certain aspects of the invention. All parts and percentages are by weight, unless otherwise noted, and all temperatures are in degrees Celsius. DADMAC was obtained from CPS Chemical Co., Inc. of Woodbridge, New Jersey. Triallylamine (TAA) was obtained from Celanese Chemical Co. VERSENE 100 was obtained from Dow Chemical Co. The hydrochloric acid and caustic were obtained from Chemtech Industries of St. Louis. The ammonium persulfate was obtained from Samirian Chemical Co. of Cupertino, California. The reagents were of commercial grade and were used as received.

## EXAMPLES

### EXAMPLE 1

A reactor was charged with the following reagents in the order given: 198 lbs. of monomer DADMAC (65 percent aqueous solution), 28 lbs. of deionized water, 0.32 lbs. of triallylamine and 0.16 lbs. of VERSENE 100 (40 percent aqueous ethylenediaminetetraacetic acid). The pH of the mixture was adjusted to 4.5 with 36 percent hydrochloric acid. A nitrogen sparge of 30 SCFH was begun, and the mixture was heated to 95°C while being agitated. A condenser was used to return any evaporated water to the reactor. After the reactor was at temperature, the nitrogen sparge was reduced to 5 SCFH with a 5 SCFH purge across the headspace. Ammonium persulfate (APS), as a 10 percent aqueous solution, was fed to

the reactor to initiate polymerization. Addition was to the surface of the stirred mixture. Initiation took place in three stages with different feed rates:

- First Feed 0.15% (wt APS/wt monomer DADMAC) over 180 minutes
- 5 Second Feed 0.15% (wt APS/wt monomer DADMAC) over 60 minutes
- Third Feed 1.2% (wt APS/wt monomer DADMAC) over 60 minutes

Beginning midway through the second feed, a 0.47 percent caustic solution was co-fed with the APS. A total of 55 lbs. of this solution was fed over 90 minutes. Caustic addition was below the surface of the stirred mixture.

- 10 At the end of the third feed, the polymerization mixture was diluted by addition of 80 lbs. of deionized water, fed over a 30-minute interval.

By this process was produced a polymer with a Brookfield viscosity of 3,450 cps at 20.2 percent solids, measured using a No. 4 spindle at 30 rpm and 25°C, and having an intrinsic viscosity of 1.53 dL/g and Huggins constant 0.52. The residual monomer content was 2.7 percent.

#### EXAMPLE 2

- 200 lbs. of monomer DADMAC (64 percent aqueous solution), 24 lbs. of deionized water, 0.32 lbs. of triallylamine, and 0.16 lbs. of VERSENE 100 were reacted as in Example 1. At the end of the third feed, the polymerization mixture was diluted by addition of 180 lbs. of deionized water, fed over a 30-minute interval. By this process was produced a polymer with a Brookfield viscosity of 4,600 cps at 20.5 percent solids, measured using a No. 4 spindle at 30 rpm and 25°C, and having an intrinsic viscosity of 1.48 dL/g and Huggins constant 0.62.
- 25 The residual monomer content was 4.0 percent.

#### EXAMPLE 3

197 lbs. of monomer DADMAC (64 percent aqueous solution), 32 lbs. of deionized water, 0.13 lbs. of triallylamine and 0.16 lbs. of VERSENE 100 were reacted as in Example 1, except that the pH of the

mixture was adjusted to 6.2 with 36 percent hydrochloric acid, and the mixture was heated to 70°C while being agitated.

At the end of the third feed, the polymerization mixture was diluted by addition of 80 lbs. of deionized water, fed over a 30-minute interval. By this process was produced a  
5 polymer with a Brookfield viscosity of 2,740 cps at 20.1 percent solids, having an intrinsic viscosity of 1.38 dL/g and Huggins constant 0.38. The residual monomer content was 4.2 percent.

The foregoing examples demonstrate that at similar concentrations of chain extender, higher molecular weight polymers can be obtained by raising the initial polymer  
10 concentration and that lowering the amount of chain extender results in a lower molecular weight polymer. In these examples, all of the chain extender is charged before polymerization is initiated. The viscosities of the polymers in examples one and two (at comparable levels of polymer solids) are higher than those of commercially available polyDADMACs prepared by solution polymerization.

15 The foregoing examples and description of the preferred embodiment should be taken as illustrating, rather than as limiting, the present invention as defined by the claims. As will be appreciated, numerous variations and combinations of the features set forth within the foregoing description and examples can be utilized without departing from the present invention.

## 20 STATEMENT OF INDUSTRIAL APPLICABILITY

The polymers of the present invention are commercially useful as flocculants and coagulants.

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**CLAIMS:**

1. A method for the preparation by solution polymerization of a polydiallyldialkylammonium salt having a predetermined molecular weight, initiated by species  
5 capable of generating free radicals, characterized by:

providing a reaction mixture of diallyldialkylammonium salt and a chain-extending monomer in aqueous solution at concentrations effective to polymerize to form a polydiallyldialkylammonium salt having a predetermined molecular weight;

adding a free radical initiator to said reaction mixture;

10 heating said reaction mixture with continuous stirring to a temperature greater than about 70°C, so that said diallyldialkylammonium salt and said chain-extending monomer polymerize to form a polydiallyldialkylammonium salt; and

recovering said polydiallyldialkylammonium salt in aqueous solution;

15 wherein the alkyl groups of said diallyldialkylammonium salt and said polydiallyldialkylammonium salt contain a total of from two to eight carbon atoms.

2. The method of claim 1, characterized in that the alkyl groups of said diallyldialkylammonium salt and said polydiallyldialkylammonium salt contain one carbon atom each.

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3. The method of claim 2, characterized in that said diallyldialkylammonium salt and said polydiallyldialkylammonium salt are chloride salts.

4. The method of claim 1, characterized in that said diallyldialkylammonium  
25 salt and said polydiallyldialkylammonium salt are chloride salts.

5. The method of claim 1, characterized in that both allylic groups of said diallyldialkylammonium salt and said polydiallyldialkylammonium salt are allyl groups.

30 6. The method of claim 1, characterized in that said chain-extending monomer is present in an amount between about 0.05 percent to about 3 percent by weight based on the amount of said diallyldialkylammonium salt.

7. The method of claim 1, characterized in that said chain-extending monomer is selected from the group consisting of triallylammonium salts, tetraallylammonium salts and N,N,N',N'-tetraallyl-(1,2)-ethylene-diammonium salts.

5 8. The method of claim 1, characterized in that said chain-extending monomer is prepared in situ by the addition of triallylamine to said reaction mixture followed by neutralization with an acid.

10 9. The method of claim 8, characterized in that said triallylamine is neutralized with hydrochloric acid to form triallylammonium chloride.

10. The method of claim 1, characterized in that said free radical initiator is a persulfate salt.

15 11. The method of claim 1, characterized in that said free radical initiator is an azo compound.

12. The method of claim 1, characterized in that said free radical initiator is added all at once at the beginning of the reaction.

20 13. The method of claim 1, characterized in that said free radical initiator is added in portions throughout the course of the reaction.

14. The method of claim 1, characterized in that said free radical initiator is added continuously throughout the course of the reaction.

15. The method of claim 1, characterized in that said reaction mixture is heated to a temperature greater than about 95°C.

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16. The method of claim 1, characterized in that said heating step comprises feeding an alkaline solution to said reaction mixture to maintain the pH of said reaction mixture between about 4 and 7 throughout the polymerization of said diallylicdialkylammonium salt and said chain-extending monomer to form said polydiallylicdialkylammonium salt.

5

17. An aqueous solution of a polydiallylicdialkylammonium salt characterized by being prepared by the method of claim 1.

18. The aqueous solution of claim 17, characterized in that said  
10 polydiallylicdialkylammonium salt is a polydiallyldimethylammonium salt.

19. The aqueous solution of claim 18, characterized in that said polydiallyldimethylammonium salt is a chloride salt.

20. The aqueous solution of claim 17, characterized in that said  
15 polydiallylicdialkylammonium salt is a chloride salt.

21. The aqueous solution of claim 17, characterized by about a 20 percent solids content and having a bulk viscosity greater than about 3,000 cps measured by a Brookfield  
20 viscometer using a No. 4 spindle at 30 rpm and 25°C.

22. A method for the separation of suspended particles from an aqueous medium, characterized by:

adding the aqueous solution of the polydiallylicdialkylammonium salt of  
25 claim 17 to said aqueous medium in an amount effective to provide a polymer concentration of at least about 0.01 weight percent, so that agglomerates of said polydiallylicdialkylammonium salt and said suspended particles are formed; and

separating said agglomerates from said aqueous medium.

23. The method of claim 22, characterized in that said  
30 polydiallylicdialkylammonium salt is a polydiallyldimethylammonium salt.

24. The method of claim 23, characterized in that said polydiallyldimethylammonium salt is a chloride salt.

25. The method of claim 22, characterized in that said  
5 polydiallyldialkylammonium salt is a chloride salt.

26. The method of claim 22, characterized in that said polydiallyldialkylammonium salt agglomerates said suspended particles by coagulation.

10 27. The method of claim 22, characterized in that said polydiallyldialkylammonium salt agglomerates said suspended particles by flocculation.

28. The method of claim 22, characterized in that the agglomerates are separated from said aqueous medium by precipitating said agglomerates, and method further  
15 includes the step of decanting the supernatant liquid essentially free of suspended particles.

29. The method of claim 22, characterized in that said suspended particles in said aqueous medium form an oil-in-water emulsion.

20 30. The method of claim 22, characterized in that said method further comprises the step of adding a second coagulant or flocculant to said aqueous medium.

31. A substrate coated with a layer of a polydiallyldialkylammonium salt characterized by being prepared by the method of claim 1.

25

32. A method for preparing a coated substrate characterized by forming on said substrate a layer of the aqueous solution of the polydiallyldialkylammonium salt of claim 171 and drying said layer.

30 33. A coated substrate characterized by being prepared by the method of claim

32.

## INTERNATIONAL SEARCH REPORT

International application No.

PC 98/21791

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C02F 1/52, 1/54; C08F 34/00

US CL : 210/716, 717, 723, 724, 728, 734, 735; 526/237, 295

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 210/716, 717, 723, 724, 728, 734, 735; 526/237, 295

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,026,794 A (MAUCERI) 31 May 1977, abstract, column 3, lines 8-58.	22-30
X	US 4,064,333 A (RABINOWITZ et al) 20 December 1977, entire document.	17,18
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A		1-16, 19-30
X	US 4,151,202 A (HUNTER et al) 24 April 1979, entire document.	1-6,10-15,17-21
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A		7-9,16,22-33
A	US 4,713,431 A (BHATTACHARYYA et al) 15 December 1987, entire document.	1-30
A	US 5,422,408 A (CRAMM et al) 06 June 1995, entire document.	1-30



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

04 JANUARY 1999

Date of mailing of the international search report

02 FEB 1999

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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/898/21791

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,653,886 A (KERR et al) 05 August 1997, entire document.	17-30
A	US 5,422,408 A (CRAMM et al) 06 June 1995, entire document.	1-30